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(54) **Gold alloys and master alloys for obtaining them**

(57) Gold alloy comprising, by weight, at least Gold $\text{Au} \geq 51\%$, Iridium $\text{Ir} \leq 0.1\%$, Germanium $\text{Ge} \leq 2\%$ and Copper $\text{Cu} \leq 45\%$. The alloy can also comprise, in percentage by weight, Silver $\text{Ag} \leq 34\%$, nickel $\text{Ni} \leq 20\%$ and Zinc $\text{Zn} \leq 12\%$. In some variations the gold alloy can further comprise no more than 4% of at least one of the elements of the group constituted by cobalt, manga-

nese, tin and indium, and no more than 0.15% of at least one of the deoxidising elements of the group constituted by magnesium, silicon, boron and lithium. To the alloy can also be added at least one of the refining elements of the group constituted by ruthenium, rhenium and platinum in quantities not exceeding 0.4% by weight. The invention further relates to a master alloy for obtaining said gold alloy.

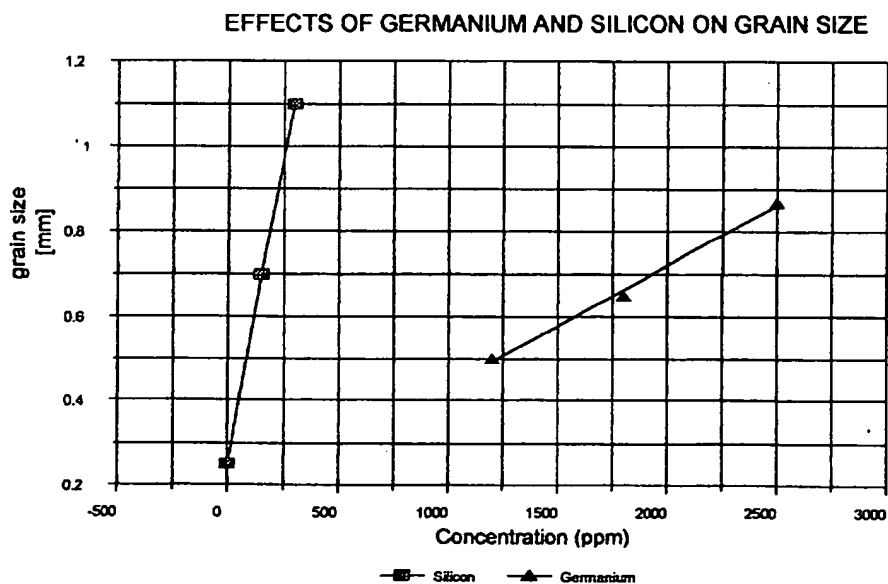


FIG. 2

Description

[0001] The present invention relates to gold alloys and to master alloys for obtaining them, mainly for the manufacture of precious objects such as jewellery and gold works, coins and medals.

[0002] One of the fundamental problems is to obtain gold alloys exhibiting good fluidity (i.e. a good ability to fill the die) at the moment of casting.

[0003] According to the procedures commonly used today, this is obtained by adding to the alloy some silicon, which, in addition to having a fluidising effect on the alloys, also has a deoxidising effect.

[0004] During the process period in which the metal remains molten, the silicon tends to combine with the oxygen present both in the starting materials and in the surrounding atmosphere.

[0005] This gives rise to a protective ability of the silicon which is manifested both during the production of granules by casting, and during the process for producing the castings comprising the melting, superheating and filling of the cavity of the mould made of refractory material.

[0006] However, the use of silicon in gold alloys also gives rise to a considerable drawback constituted by the fact that these alloys exhibit, once solidified, a crystal grain of relatively large size, with a consequent degradation of the mechanical properties (especially in the case of 18 carat gold alloys), and a consequent undesired fragility of the pieces themselves.

[0007] Given this problem, one route followed by industry operators, to decrease grain size, has been to add to the alloys also a suitable quantity of elements such as iridium, ruthenium, cobalt, nickel and rhodium, which tend to refine crystal grain.

[0008] However, this solution too is not wholly free of drawbacks.

[0009] In the first place, silicon tends to combine with the refining elements commonly used giving rise to the formation of silicides which go to constitute spheroidal conglomerates of inter-metallic compounds with high hardness, originating flaws known as "hard spots".

[0010] Such inclusions can appear on the surface of the finished piece after the final work process, entailing either the rework of the piece, or its discarding.

[0011] In this situation the technical task constituting the basis of the present invention is to provide gold alloys and master alloys for obtaining them which overcome the aforementioned drawbacks.

[0012] In particular the technical task of the present invention is to provide gold alloys and master alloys for obtaining them which exhibit an excellent fluidity in the molten state even without silicon additions.

[0013] The specified technical task and the indicated aims are substantially achieved by gold alloys and master alloys for obtaining them, as described in the accompanying claims.

[0014] An alternative element to silicon is germanium

which, in the percentage of employment described in the present invention, has very distinct fluidising properties, superior to those of silicon: as described below, this feature is readily apparent in comparative melting tests between silicon based alloys and germanium based alloys, the latter described in the present invention.

[0015] In addition, the bath of germanium based alloys exhibits an extremely clean, slag-free surface, characteristic that is due to the fact that the germanium oxides which may be present on the surface of the bath are removed by sublimation at temperatures f around 710°C . Relative to silicon based alloys, therefore, the possibility of inclusions of oxide particles in the castings, with the consequent risk of brittleness, is drastically reduced.

[0016] Moreover, it has also been verified that germanium concentrations varying between 0.05% and 2% by weight have led to an increase in fluidity deemed to be even greater than the one provided by silicon in normal usage concentrations, whilst exhibiting an increase in grain size, following such addition, that is decidedly smaller than that observed in silicon alloys. Hence, in the case of germanium alloys, with low or nil silicon content, in addition to the fluidising effect obtained, exceeding that of silicon, the mechanical characteristics of the alloy are improved as well, as can be observed from the data illustrated below.

[0017] Moreover, a noticeable ameliorating effect of germanium has been observed on the ductility of the alloy obtained, superior to the effect of silicon.

[0018] Of interest is also the combined use of germanium and small quantities of silicon: this combination allows to obtain "clean and shiny" castings, without causing the immediate degradation of the mechanical properties as can be observed with the use of silicon alone in greater quantities.

[0019] One thereby also avoids the problem of the formation of hard spots, harmful when polishing the finished pieces, avoiding the insertion in the alloy of refining elements (with the aim of bringing mechanical properties back to functional values) such as cobalt and nickel.

[0020] The ameliorative effect of germanium on mechanical properties can also be exhibited in nickel based white alloys, as is evident from the formulations described hereafter.

[0021] Further characteristics and the advantages of the present invention shall become more readily apparent from the detailed description of some preferred, but not exclusive, embodiments of gold alloys and master alloys for obtaining them, and from the accompanying figures, in which:

- Figure 1 shows in graph form the effect of different elements and compounds on the grain size of a gold alloy;
- Figure 2 shows in graph form the effect of the quantity of silicon and germanium on the grain size of the

- gold alloy;
- Figure 3 shows in graph form the effect of the elements and compounds of Figure 1 on the maximum load bearable by the gold alloy obtained therewith;
- Figure 4 shows in graph form the effect of the elements and compounds of Figure 1 on the ductile properties (lengthening as a result of traction) of the alloy.

[0022] The gold alloy of the present invention comprises at least the following elements:

- gold: $Au \geq 51 \%$;
- iridium: $Ir \leq 0.2 \%$;
- germanium: $Ge \leq 2 \%$;
- copper: $Cu \leq 45 \%$, and in any case sufficient to reach 100, in the indicated quantities, with reference to the total weight of the alloy.

[0023] As stated, the fundamental characteristic of said alloy is that of containing germanium as a fluidising element, while being able to be free of silicon.

[0024] The better to meet particular productive requirements, to complete the alloy several other chemical elements can also be used.

[0025] In particular, depending on requirements, the gold alloy can contain (with percentages expressed in weight):

- silver: $Ag \leq 34 \%$;
- nickel: $Ni \leq 20 \%$;
- zinc: $Zn \leq 12 \%$, which can be present simultaneously, or otherwise, without thereby departing from the scope of the present invention.

[0026] In particular, the addition of nickel (or other elements having similar properties, and equivalent thereto) in suitable quantity, allows to obtain alloys of so-called white gold.

[0027] Secondly, the alloy can also contain, in a proportion not exceeding 4% by weight, at least one of the elements of the group constituted by cobalt, manganese, tin and indium.

[0028] To improve the qualities of the alloy, one or more deoxidising elements such as magnesium, silicon, boron and lithium can also be added, each in a proportion not exceeding 0.15% by weight.

[0029] Note that, even when silicon is added to the alloy, it is added only in small quantities (in particular not exceeding 0.05% by weight in 18 carat alloys, and not exceeding 0.15% by weight in 14 carat alloys) solely in order to guarantee the protection of the alloy against the formation of oxides, and not to improve its fluidity.

[0030] Due to particular productive requirements in which a particularly reduced grain size is required, the alloy can also comprise refining elements such as ruthenium, rhenium and platinum in a suitable quantity and preferably not exceeding 0.4% by weight.

[0031] For the production of precious objects, moreover, there are two preferential ranges for the quantity of gold present in the alloy.

[0032] A first preferred range is the one associated with obtaining 18 carat gold, in which the quantity of gold present in the alloy is between 74% and 77% by weight.

[0033] A second preferred range is the one associated with obtaining 14 carat gold, in which the quantity of gold present in the alloy is between 57% and 60% by weight.

[0034] In regard to master alloys for obtaining the above gold alloys, they are composed at least by:

iridium: $Ir \leq 0.4 \%$;
germanium $Ge \leq 4 \%$;
copper: Cu sufficient to reach 100,

in the indicated quantities, with reference to the total weight of the master alloy.

[0035] Moreover, as stated, the master alloy can also comprise, as a weight percentage relative to the total weight of the master alloy:

silver: $Ag \leq 72 \%$;
nickel: $Ni \leq 41 \%$;
zinc: $Zn \leq 25 \%$.

[0036] Additionally, the master alloy can include, in quantities not exceeding 8% by weight, at least one of the elements of the group constituted by cobalt, manganese, tin and indium.

[0037] The master alloy can further include, in quantities not exceeding 0.36% by weight, at least one of the deoxidising elements of the group constituted by magnesium, silicon, boron and lithium.

[0038] Advantageously, in some applications, at least one of the refining elements of the group constituted by ruthenium, rhenium and platinum can be inserted in the master alloy, in quantities not exceeding 0.96% by weight.

[0039] Some examples of gold alloys which can be obtained with a composition in accordance with the present invention are set out below.

Example A.

[0040] 14 carat yellow gold alloy whose composition in terms of weight percentage is as follows:

Gold	58.5
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with master alloy comprising (as a percentage on the weight of the gold alloy):

Silver	8.0
Zinc	6.0
Iridium	0.01

(continued)

Germanium	0.4
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[0041] Copper, sufficient to reach 100 (in this specific case, 27.09%).

Example B

[0042] 18 carat yellow gold alloy whose composition in terms of weight percentage is as follows:

Gold	75.0
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with master alloy comprising (as a percentage on the weight of the gold alloy):

Silver	15.0
Iridium	0.01
Germanium	0.2.

[0043] Copper sufficient to reach 100 (in this specific case 9.79%)

Example C

[0044] 18 carat yellow gold alloy whose composition in terms of weight percentage is as follows:

Gold	75.0
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with master alloy comprising (as a percentage on the weight of the gold alloy):

Silver	12.5
Zinc	0.5
Germanium	0.25
Silicon	0.04.

[0045] Copper sufficient to reach 100 (in this specific case 11.71%).

Example D

[0046] 14 carat white gold alloy whose composition in terms of weight percentage is as follows:

Gold	58.5
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with master alloy comprising (as a percentage on the weight of the gold alloy):

Nickel	8.5
Zinc	8.0
Iridium	0.01

(continued)

Germanium	0.4.
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[0047] Copper sufficient to reach 100 (in this specific case 24.59%).

Example E

[0048] 18 carat white gold alloy whose composition in terms of weight percentage is as follows:

Gold	75.0
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with master alloy comprising (as a percentage on the weight of the gold alloy):

Nickel	7.5
Zinc	3.5
Iridium	0.01
Germanium	0.25.

[0049] Copper sufficient to reach 100 (in this specific case 13.74%).

[0050] To obtain the three yellow gold alloys described in examples A, B and C set out above, a preferential process comprises the following phases:

- melting in controlled atmosphere or in an inert gas such as argon, of the elements in the respective doses, inside graphite or ceramic crucibles at a temperature ranging between 880 and 940°C;
- subsequent heating to a temperature ranging between 970 and 1030 °C before proceeding with casting;
- casting the material in appropriate dies;
- cooling the die in air;
- subsequent cooling of the die in water.

To obtain instead the two white gold alloys described in examples D and E, set out above, a preferential process comprises the following phases:

- melting in controlled atmosphere or in an inert gas such as argon, of the elements in the respective doses, inside graphite or ceramic crucibles at a temperature ranging between 890 and 970°C;
- subsequent heating to a temperature ranging between 980 and 1100 °C before proceeding with casting;
- casting the material in appropriate dies;
- cooling the die in air;
- subsequent cooling of the die in water.

[0051] The present invention achieves important advantages.

[0052] In the first place, laboratory tests conducted by

the Applicant have shown that use of Germanium in weight concentrations ranging between 0.05% and 2% leads to an increase in the fluidity of the alloy in the molten state that is even greater than the one brought about by the use of silicon in normal usage concentrations.

[0053] Moreover, the increase in grain size consequent to the use of germanium was lesser than the one that takes place in traditional alloys containing silicon, as shown in Figures 1 and 2.

[0054] Figure 1 shows the variation in the dimensions of the crystal grain of the alloy as a result of the addition, thereto, of the elements and compounds indicated in the x-coordinate. It is evident that the influence of Silicon (CuSi) on the increase in grain size is considerably lesser than the influence of Germanium (Ge).

[0055] Figure 2 shows the effect of the concentration of Silicon and germanium on the grain dimension of the gold alloy. In this case, too, it is evident that a low concentration of silicon, in the graph from 0 to 300 ppm, entails a considerable increase in crystal grain size, even exceeding the size increase caused by additions of germanium in concentrations that are 10 times greater.

[0056] This has positive repercussions on the mechanical behaviour of the alloy, as can be seen in Figure 3, which shows the (positive or negative) variation of the maximum load (measured with a traction test) bearable by the alloy, following the addition to the alloy of equal quantities of the different elements or compounds indicated in the x-coordinate.

[0057] Figure 4 shows the percent variation of the lengthening of the gold alloy subjected to traction test, as a function of the addition to the alloy of the elements and compounds, indicated in the x-coordinate, in equal quantities.

[0058] The use of germanium instead of silicon also yielded positive effects on the percent of lengthening of the alloy following the traction test.

[0059] In regard to the combined use of germanium and silicon, respectively to improve the fluidity and decrease the oxidation of the alloy, very encouraging results were obtained.

[0060] The combined use of these two elements gave rise to deoxidised alloys which at the same time show a very good mechanical behaviour, generally better than the one exhibited by the alloys in which silicon is used both as a fluidising element, and as a deoxidising element.

[0061] Moreover, the alloys obtained according to the present invention (be they gold alloys or master alloys for obtaining gold alloys), thanks to the small size of the crystal grain, are normally able not require the use of other refining elements.

[0062] In any case, where the use of refining elements becomes necessary to obtain even smaller grain dimensions, the formation of silicides does not take place, thanks to the absence, or near absence, of silicon.

[0063] It should further be noted that the present in-

vention is relatively easy to implement and that also the cost connected to the implementation of the invention remains within the standards of the industry.

[0064] The invention thus conceived can be subject to numerous modifications and variations, without thereby departing from the scope of the inventive concept that characterises it.

10 Claims

1. Gold alloy **characterised in that** it comprises, in terms of weight, at least:

15 Gold: $Au \geq 51 \%$;
Iridium: $Ir \leq 0.2 \%$;
Germanium: $Ge \leq 2 \%$;
Copper: $Cu \leq 45 \%$.

20 2. Gold alloy as claimed in claim 1 **characterised in that** it further comprises silver with a percentage by weight of: $Ag \leq 34 \%$.

3. Gold alloy as claimed in any of the previous claims **characterised in that** it further comprises Nickel with a percentage by weight of: $Ni \leq 20 \%$.

4. Gold alloy as claimed in any of the previous claims **characterised in that** it further comprises Zinc with a percentage by weight of: $Zn \leq 12 \%$.

5. Gold alloy as claimed in any of the previous claims **characterised in that** it comprises Gold with a percentage by weight of: $74 \leq Au \leq 77 \%$.

6. Gold alloy as claimed in any of the claims from 1 to 5 **characterised in that** it comprises Gold with a percentage by weight of: $57 \leq Au \leq 60 \%$.

7. Gold alloy as claimed in any of the previous claims **characterised in that** it further comprises no more than 4 % by weight of at least one of the elements of the group constituted by cobalt, manganese, tin and indium.

8. Gold alloy as claimed in any of the previous claims **characterised in that** it further comprises no more than 0.15 % by weight of at least one of the elements of the group constituted by magnesium, silicon, boron and lithium.

9. Gold alloy as claimed in any of the previous claims **characterised in that** it further comprises no more than 0.4 % by weight of at least one of the elements of the group constituted by ruthenium, rhenium and platinum.

10. Gold alloy for obtaining gold alloys as claimed in any

of the previous claims **characterised in that** it comprises, by weight, at least:

Iridium: Ir ≤ 0.4 %;
Germanium: Ge ≤ 4 %; 5
Copper: Cu sufficient to reach 100.

11. Master alloy as claimed in claim 10 **characterised in that** it further comprises Silver with a percentage by weight of: Ag ≤ 72 %. 10
12. Master alloy as claimed in either of the claims 10 or 11 **characterised in that** it further comprises nickel with a percentage by weight of: Ni ≤ 41 %. 15
13. Master alloy as claimed in any of the claims from 10 to 12 **characterised in that** it further comprises Zinc with a percentage by weight of: Zn ≤ 25 %.
14. Master alloy as claimed in any of the claims from 10 to 13 **characterised in that** it further comprises no more than 8 % of at least one of the elements of the group constituted by cobalt, manganese, tin and indium. 20
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15. Master alloy as claimed in any of the claims from 10 to 14 **characterised in that** it further comprises no more than 0.36 % of at least one of the elements of the group constituted by magnesium, silicon, boron and lithium. 30
16. Master alloy as claimed in any of the claims from 10 to 15 **characterised in that** it further comprises no more than 0.96 % by weight of at least one of the elements of the group constituted by ruthenium, rhenium and platinum. 35

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EFFECTS OF ELEMENTS ON GRAIN SIZE

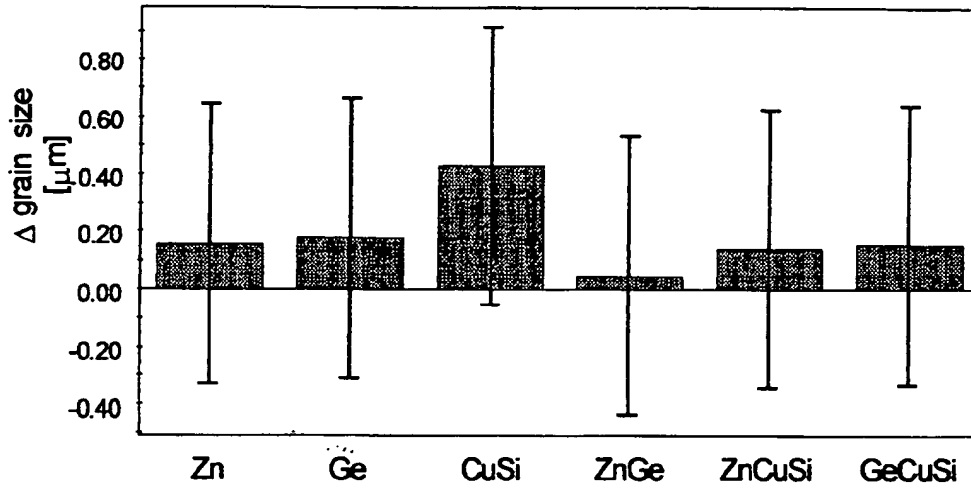


FIG. 1

EFFECTS OF GERMANIUM AND SILICON ON GRAIN SIZE

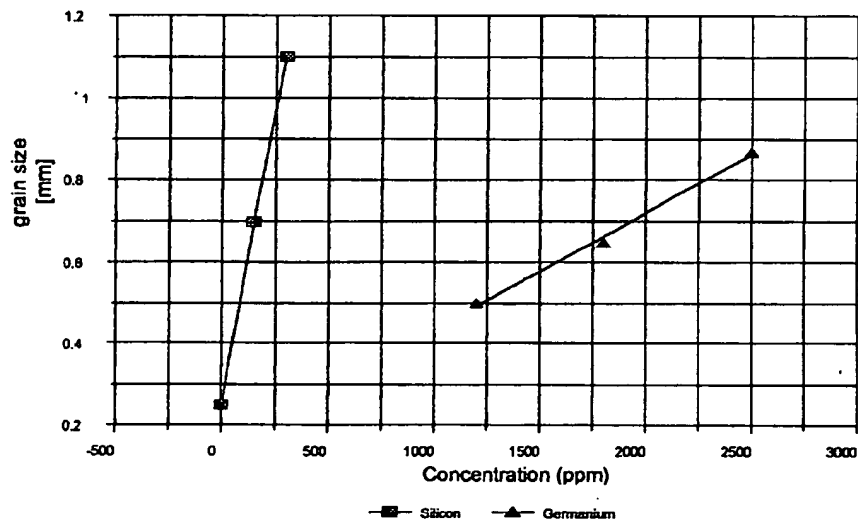


FIG. 2

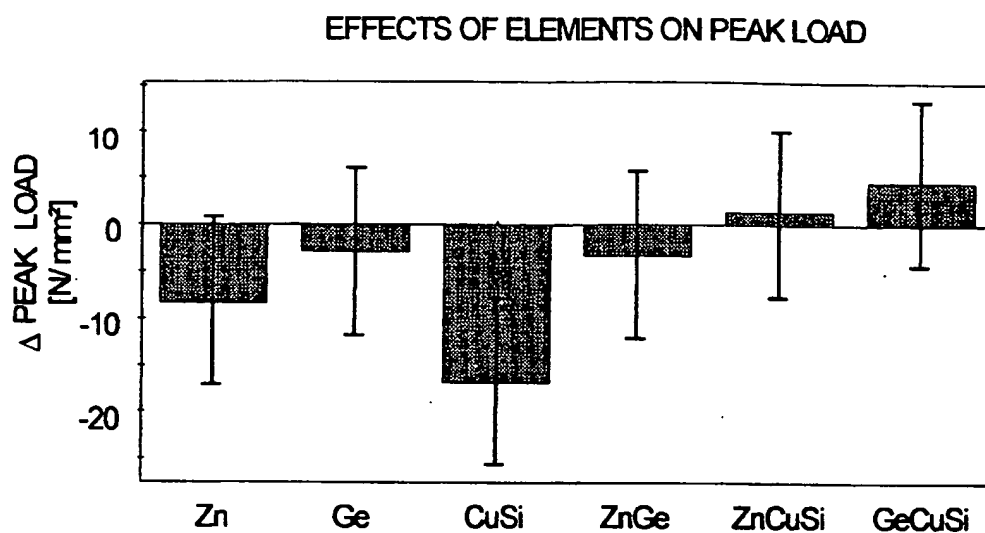


FIG. 3

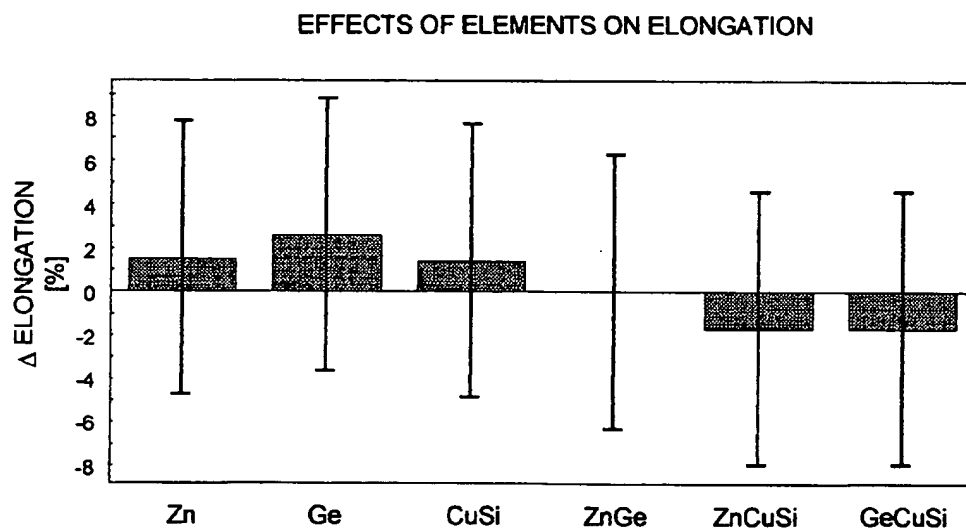


FIG. 4



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EUROPEAN SEARCH REPORT

Application Number
EP 01 83 0349

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 444 (C-545), 22 November 1988 (1988-11-22) -& JP 63 169347 A (TOKURIKI MONTEN CO LTD), 13 July 1988 (1988-07-13) * abstract *	1-16	C22C9/05
X	EP 0 381 994 A (HAFNER C GMBH & CO) 16 August 1990 (1990-08-16) * page 2, 1.35-36; example 11 *	1-4,7-16	
X	DE 43 20 928 C (HERAEUS KULZER GMBH) 17 March 1994 (1994-03-17) * abstract; example F *	1-16	
X	DE 30 19 277 A (WIELAND FA DR TH) 26 November 1981 (1981-11-26) * claim 1; page 4, last paragraph *	1-16	
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 12, 25 December 1997 (1997-12-25) -& JP 09 209060 A (SUMITOMO METAL MINING CO LTD), 12 August 1997 (1997-08-12) * abstract *	1-4,7-16	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C22C
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 04, 30 April 1999 (1999-04-30) -& JP 11 000792 A (SUMITOMO METAL MINING CO LTD), 6 January 1999 (1999-01-06) * abstract *	1-4,7-16	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 10 October 2001	Examiner Bjoerk, P
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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Application Number
EP 01 83 0349

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 02, 31 March 1995 (1995-03-31) -& JP 06 330206 A (NIPPON STEEL CORP), 29 November 1994 (1994-11-29) * abstract * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 10 October 2001	Examiner Bjoerk, P
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 (3.0.02) (P04C01)

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ON EUROPEAN PATENT APPLICATION NO.**

EP 01 83 0349

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10-10-2001

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
JP 63169347	A	13-07-1988	NONE		
EP 0381994	A	16-08-1990	DE 59009704 D1		02-11-1995
			EP 0381994 A1		16-08-1990
DE 4320928	C	17-03-1994	DE 4320928 C1		17-03-1994
DE 3019277	A	26-11-1981	DE 3019277 A1		26-11-1981
JP 09209060	A	12-08-1997	NONE		
JP 11000792	A	06-01-1999	NONE		
JP 06330206	A	29-11-1994	NONE		

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82